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Contract N/N00014-91-J-1893
R&T Code 4132062

TECHNICAL REPORT NO. 11

Preparation of Homogeneous Aluminosilicate Gels by
Sol/Gel Techniques

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July 12, 1993

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93-16241



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REPORT DOCUMENTATION PAGE

FORM 298-100
1-79

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 7/12/93	3. REPORT TYPE AND DATES COVERED Technical	
4. TITLE AND SUBTITLE Preparation of Homogeneous Aluminosilicate Gels by Sol/Gel Techniques			5. FUNDING NUMBERS N/N00014-91-J-1893	
6. AUTHOR(S) M.E. Reese, J. Sanchez and A.V. McCormick				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Dept. of Chemical Engineering & Materials Science University of Minnesota 421 Washington Ave., SE Minneapolis, MN 55455			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Street Arlington, VA 22217			10. SPONSORING MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Published in Proceedings, MRS Meeting, Fall 1991 #28				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the U.S. Government. This document has been approved for public release and sale; its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The factors affecting the production of homogeneous aluminosilicate gels from alkoxide precursors were investigated. Aluminosilicate gels were made in acidic conditions with a prepolymerization of the silicate precursors followed by the addition of the alumina precursor. Confirming earlier studies, we found that the gel homogeneity is increased when the rate of gelation decreases. The reduction of the water content and/or the aluminum precursor, and more surprisingly the increase of the acid concentration contributed to the gel time increase and thus the improvement of gel homogeneity.				
14. SUBJECT TERMS Sol/gel, NMR, Al_2O_3 , SiO_2			15. NUMBER OF PAGES 6	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT UL	

Published in Polymer Preprints, Vol. 1, No. 1, 1980
28
Revised w/

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SOL/GEL TECHNIQUES

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ABSTRACT

The factors affecting the production of homogeneous aluminosilicate gels from alkoxide precursors were investigated. Aluminosilicate gels were made in acidic conditions with a prepolymerization of the silicate precursor followed by the addition of the alumina precursor. Confirming earlier studies, we found that the gel homogeneity is increased when the rate of gelation decreases. The reduction of the water content and/or the aluminum precursor, and more surprisingly the increase of the acid concentration contributed to the gel time ~~decrease~~ and thus the improvement of gel homogeneity .

INTRODUCTION

Sol/gel processing offers many advantages over more traditional processing techniques to produce polymeric aluminosilicate gels. The chief advantage of the molecular-scale homogeneity possible through sol/gel processing is that one can in principle produce aluminosilicates with any arbitrarily specified composition, so one can tailor physico-chemical properties which are extremely sensitive to the composition on the molecular scale.

However, not all sol/gel techniques work; on the contrary, it is quite difficult to produce homogeneous aluminosilicate polymers. It is the purpose of this paper to study the factors affecting the gel homogeneity.

HOMOGENEITY OF ALUMINOSILICATE GELS

The degree of homogeneity ideally attained in a gel is the *molecular homogeneity*. For an aluminosilicate gel, this would correspond to a high concentration of Al-O-Si bonds produced by copolymerization of the silicon alkoxide and aluminum alkoxide precursors. However, the homopolymerization of aluminates is much faster than both the silica homopolymerization and the alumina-silica copolymerization, yielding a separation of alumina and silica-rich phases. Typically, this results in the formation of colloids or even precipitates, instead of gels. Even if a gel is produced, it is cloudy and opaque. The use of double alkoxides (Pouxviel, Yasumori), e.g. $(\text{BuO})_2\text{-Al-O-Si-(OEt)}_3$, could in principle improve the homogeneity, but Pouxviel et al. have observed that even for these precursors, only certain regions of sol/gel solution composition yield homogeneous gels, and these compositions correspond to extremely slow gel times.

A good indication of the homogeneity of a gel is its *macroscopic homogeneity* which will concern us here. It does not however necessarily implies homogeneity at the molecular level. Macroscopically homogeneous gels appear transparent to the eye, and exempt of precipitates or any visible phase separation.

EXPERIMENTAL

The ceramic precursors were silicon tetraethoxide or TEOS ($\text{Si}[\text{EtO}]_4$) and aluminum sec-butoxide ($[\text{sec-C}_4\text{H}_9\text{O}]_3\text{Al}$). This aluminum precursor proved to be much superior to aluminum isopropoxide to obtain homogeneous gels. In addition, aluminum isopropoxide does not readily dissolve in ethanol, isopropanol or 1-butanol.

The method that gave the best product was adapted from a process described by Krol (Krol). To reduce the reactivity difference between the silicon and aluminum alkoxides, TEOS was "prehydrolyzed": 30 ml

TEOS were dissolved in 31.5 ml absolute ethanol. 3ml of water with various HCl concentration was then added. At this point, the molar ratio $\text{TEOS}/\text{H}_2\text{O}$ is thus 1/1.2. This mixture was left at 50°C under vigorous stirring for 10 minutes. After cooling (5 mn in ice bath), stirring was resumed and the aluminum precursor was added. Finally, after 5 minutes, the remaining water was slowly added. Stirring was then stopped and the system was left to gel.

RESULTS

The effect of three factors -the water content, the aluminum precursor content and the acid concentration, on the gel time and gel macroscopic homogeneity was studied.

Figure1 shows the effect of the water content. It is clear that the reduction of the water content increases the gel time and at the same time improves the gel homogeneity.

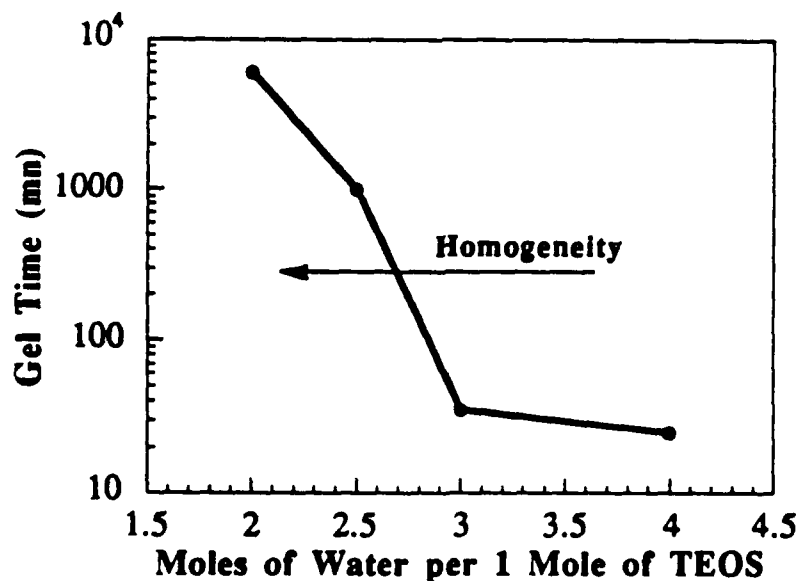


Figure 1. Effect of the water content for the system $\text{TEOS}/\text{Al}(\text{BuO})_3/\text{EtOH} = 1/0.25/4$.

Figure 2 shows that as expected, decreasing the aluminum precursor content decreases the gel time, and this again has the effect of improving the gel homogeneity. The most homogeneous gels were obtained for aluminum butoxide/TEOS ratios of less than 0.5. At higher ratios, some precipitation begins to appear.

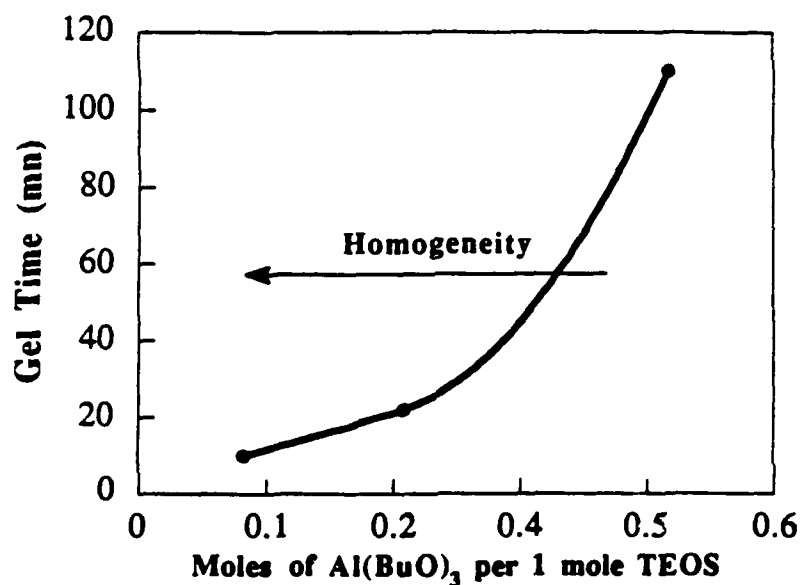


Figure 2. Effect of the Al(BuO)₃ concentration on the gel homogeneity and gelation time. System TEOS/EtOH/H₂O/HCL = 1/4/4/0.006 at 25°C.

Finally, the dependence of the gel time with the the acid catalyst content is represented in Figure 3.

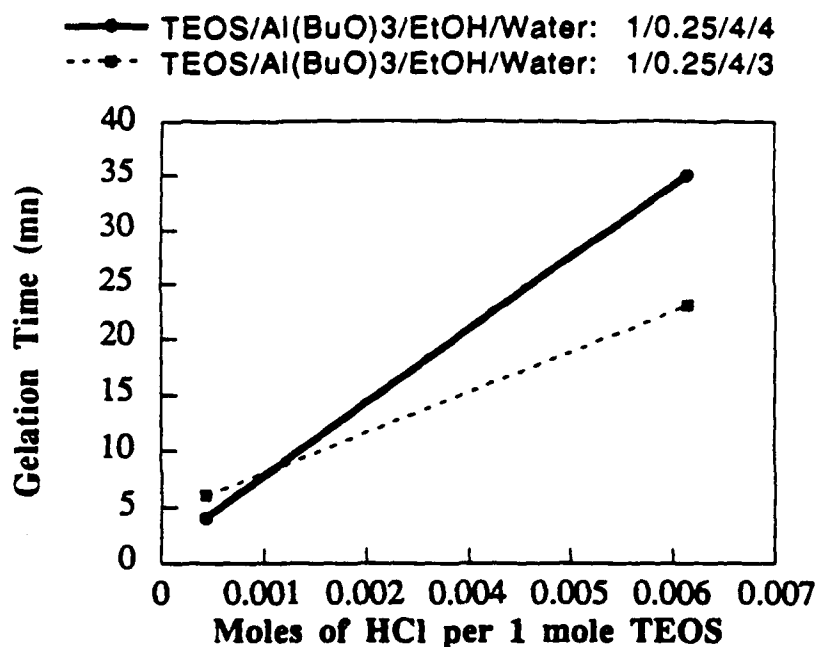


Figure 3. Effect of the acid concentration on the gel time.

Unlike what was expected, increasing the acid content of the system increases the gel time. This results again in a more homogeneous gel. If no catalyst is added, an extensive amount of phase separation is observed and a white opaque colloidal gel is formed.

DISCUSSION

The clear result is that the homogeneity of the gel is increased by decreasing the gelation rate, a result confirming previous studies (Yoldas). In a recent review on aluminosilicate gels, McCormick has explored possible reasons for the fact that decreasing the rate of gelation should increase the selectivity to copolymerization and result in a better homogeneity. He showed that this is indeed possible when the *silicate prepolymerization* (taking place in the "prehydrolyzing" step) is taken into account. "Prehydrolyzing" the silicon alkoxide has thus a more important role than just simply

reducing the kinetic reactivity differential with the aluminum precursor.

More puzzling is the counterintuitive result that increasing the acid concentration resulted in an increased gel time. Because the acid is added in the "prehydrolyzing" step, adding more acid result in a more extensive silicon prepolymerization. This confirms again the importance of the prepolymerization step in the overall process. More work is needed to accurately determine the intermediates formed in the system during the "prehydrolyzing" step and their role in the aluminosilicate gelation.

ACKNOWLEDGEMENT

This work was supported by the Office of Naval Research and by the Center for Interfacial Engineering at the University of Minnesota.

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